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Assembly of Azido- or Cyano-Bridged Binuclear Complexes Containing the Bulky $[Mn(phen)_2]^{2+}$ Building Block: Syntheses, Crystal Structures, and Magnetic Properties

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Two new cyano-bridged heterobinuclear complexes, $[Mn^{II}(phen)_2Cl][Fe^{III}(bpb)(CN)_2]\cdot 0.5CH_3CH_2OH\cdot 1.5H_2O$ (**1**) and $[Mn^{II}(phen)_2Cl][Cr^{III}(bpb)(CN)_2]\cdot 2H_2O$ (**2**) [phen = 1,10-phenanthroline; bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)-benzenate], and four novel azido-bridged Mn(II) dimeric complexes, $[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][M^{III}(bpb)(CN)_2]_2\cdot H_2O$ [M = Fe (**3**), Cr (**4**), Co (**5**)] and $[Mn_2(phen)_4(\mu_{1,3}\text{-}N_3)(N_3)_2]BPh_4\cdot 0.5H_2O$ (**6**), have been synthesized and characterized by single-crystal X-ray diffraction analysis and magnetic studies. Complexes **1** and **2** comprise $[Mn(phen)_2Cl]^+$ and $[M(bpb)(CN)_2]^-$ units connected by one cyano ligand of $[M(bpb)(CN)_2]^-$. Complexes **3**–**5** are doubly end-on (EO) azido-bridged Mn(II) binuclear complexes with two $[M(bpb)(CN)_2]^-$ molecules acting as charge-compensating anions. However, the Mn(II) ions in complex **6** are linked by a single end-to-end (EE) azido bridging ligand with one large free BPh_4^- group as the charge-balancing anion. The magnetic coupling between Mn(II) and Fe(III) or Cr(III) in complexes **1** and **2** was found to be antiferromagnetic with $J_{MnFe} = -2.68(3)$ cm^{-1} and $J_{MnCr} = -4.55(1)$ cm^{-1} on the basis of the Hamiltonian $\hat{H} = -J\hat{S}_{Mn}\hat{S}_M$(M = Fe or Cr). The magnetic interactions between two Mn(II) ions in **3**–**5** are ferromagnetic in nature with the magnetic coupling constants of 1.15(3), 1.05(2), and 1.27(2) cm^{-1} ($\hat{H} = -J\hat{S}_{Mn1}\hat{S}_{Mn2}$), respectively. The single EE azido-bridged dimeric complex **6** manifests antiferromagnetic interaction with $J = -2.29(4)$ cm^{-1} ($\hat{H} = -J\hat{S}_{Mn1}\hat{S}_{Mn2}$). Magneto-structural correlationship on the EO azido-bridged Mn(II) dimers has been investigated.

Introduction

Much attention has recently been given to the study of the magnetic interactions and magneto-structural correlations in molecular systems (mainly coordination compounds) for the purpose of exploiting new molecule-based magnetic materials and interesting multifunctional molecule-based materials.[1,2] Among them, cyano- and azido-bridged complexes have received a lot of attention because cyano and azido bridges can effectively transmit magnetic coupling and can yield a variety of molecular structures over a wide range of dimensionalities including binuclear and polynuclear complexes[3−11] and one-dimensional (1D) chainlike complexes,[12−19] as well as two- and three-dimensional networks[20−25] with fascinating magnetic properties such as

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single-moleculemagnets and single-chain magnets, high critical temperature magnetic materials, spin-crossover materials, and multifunctional materials.[7b,15]

Compared to the cyano group, the azido ligand has more linking modes and manifests more diversity in magnetism.[26] In general, there are two typical coordination modes for an azido ion acting as the bridging ligand: end-to-end (EE or μ-1,3) and end-on (EO or μ-1,1). Furthermore, it has been proven that the EE linking mode usually leads to antiferromagnetic interaction, whereas the EO mode leads to ferromagnetic interaction. However, there are some exceptions[27−29] because the magnetic coupling for the EE bridging fashion may be reversed when the bonding parameters or metal ion centers change. Interestingly, the azido group often coexists in different bridging fashions or with other bridging groups such as cyano, oxalato, carboxylato, phenolate oxygen, and 4,4′-bipy as well as diazine,[30−33] yielding novel but very complicated magnetic properties. Undoubtedly, the elucidation of the factors that affect the superexchange interaction through the azido bridge is necessary for the design of new magnetic materials.[26]

Up to now, there have been many reports on Cu^{II}− and Ni^{II}−azido systems[16,17,26,32−35] as well as Mn^{II}−azido polymeric systems[18,19,36−38] with uniform or alternating EE and EO bridges, prompting many theoretical studies[39−41] on the

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magnetic behaviors based mainly on $Cu^{II}-$ and $Ni^{II}-$azido dimeric complexes. However, to the best of our knowledge there are only seven examples of $Mn^{II}-$azide polynuclear complexes including $[Na_2Mn_2(pyz)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2(H_2O)_4]$ (pyz = 2-pyrazinic acid),[42] $[Mn_2(terpy)_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2]\cdot 2H_2O$ (terpy = terpyridine),[43] $[Mn_2(2,2'\text{-dpa})_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2]$ (2,2′-dpa = 2,2′-dipicolylamine),[44a] $[Mn_2(L)_2(\mu_{1,1}\text{-}N_3)_2](ClO_4)_2$ (L stands for three tetradentate ligands)[44b] and $[Mn_2(bpy)_4(\mu_{1,3}\text{-}N_3)_2](ClO_4)_2\cdot bpy$ (bpy = 2,2′-bipyridine)[26] dimers, and there have been no reports of a Mn(II) binuclear complex bridged by a single EE azide bridge. Similar to bpy, the ligand 1,10-phenanthroline (phen) can coordinate to the Mn(II) ion to form stable complexes. However, only the mononuclear complex $Mn(phen)_2(N_3)_2$ has been obtained by the reaction of MnX_2 ($X = Cl^-$, ClO_4^-), phen, and NaN_3 in the molar ratio of 1:2:excess.[45] With the hope of obtaining azido-bridged $Mn(phen)_2^{2+}$ complexes, others have tried using less NaN_3 ($Mn^{2+}/N_3^- = 1:1$) in the presence of an excess of $NaClO_4$; however, another mononuclear $[Mn(phen)_2(N_3)(H_2O)]ClO_4$ was obtained.[45a] Very recently, oxalate-bridged binuclear $[(phen)(C_2O_4)Cr(\mu\text{-}C_2O_4)Mn(phen)_2(N_3)]\cdot H_2O$[46] has been obtained, which contains a terminal azido ligand. It appears that it is impossible to synthesize azido-bridged complexes based on the $Mn(phen)_2^{2+}$ building block. In this work, we have successfully synthesized three new azido-bridged Mn(II) binuclear complexes, three isostructural $[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][M(bpb)(CN)_2]_2\cdot H_2O$ [M = Fe (**3**), Cr (**4**), and Co (**5**); bpb = 1,2-bis(pyridine-2-carboxamido)benzene] complexes, and $[Mn_2(phen)_4(\mu_{1,3}\text{-}N_3)(N_3)_2]BPh_4\cdot 0.5H_2O$ (**6**). Complex **6** is an interesting example that contains a single EE azido bridge that has never been observed before. Herein, we report the syntheses, crystal structures, and magnetic properties of the azido-bridged dimers together with two cyano-bridged dimeric complexes, $[Mn(phen)_2Cl][Fe(bpb)(CN)_2]\cdot 0.5CH_3CH_2OH\cdot 1.5H_2O$ (**1**) and $[Mn(phen)_2Cl][Cr(bpb)(CN)_2]\cdot 2H_2O$ (**2**), which were obtained in the absence of N_3^-.

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000−400 cm^{-1} regions. Variable-temperature magnetic susceptibilities were performed in an applied field of 2000 Oe on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Syntheses. The precursors $Mn(phen)_2Cl_2$, $K[Fe(bpb)(CN)_2]$, $K[Co(bpb)(CN)_2]$, and $K[Cr(bpb)(CN)_2]$ were prepared according to literature methods.[47−49]

Caution! Perchlorate and azide salts of metal complexes are potentially explosive and should be handled in small quantities with care.

$[Mn(phen)_2Cl][Fe(bpb)(CN)_2]\cdot 0.5CH_3CH_2OH\cdot 1.5H_2O$ (1) and $[Mn(phen)_2Cl][Cr(bpb)(CN)_2]\cdot 2H_2O$ (2). Deep reddish brown block single crystals of **1** and dark red block single crystals of **2** were obtained by the slow reaction of $Mn(phen)_2Cl_2$ (0.1 mmol, 30.6 mg) and $K[M(bpb)(CN)_2]$ [M = Fe (**1**), Cr (**2**)] (0.1 mmol) in a methanol, ethanol, acetonitrile, and water mixing solution (10 mL) after ∼1 day. Yield: 50.8 mg (55.1%) for **1** and 45.2 mg (49.8%) for **2**. Anal. Calcd for $C_{45}H_{34}N_{10}O_4ClFeMn$ (**1**): C, 58.43; H, 3.70; N, 15.14. Found: C, 57.78; H, 4.02; N, 14.75. Selected IR frequencies (KBr disk, cm^{-1}): 2127 (m, $\nu_{C\equiv N}$), 2116 (m, $\nu_{C\equiv N}$), 1618 (vs, $\nu_{C=O}$), 1591 (vs), 1515 (m), 1469 (m), 1423 (m), 1358 (s), 1138 (m), 847 (m), 764 (s), 729 (m), 690 (m), 506 (m). Anal. Calcd for $C_{44}H_{32}N_{10}O_4ClCrMn$ (**2**): C, 58.26; H, 3.56; N, 15.44. Found: C, 57.83; H, 3.84; N, 15.10. Selected IR frequencies (KBr disk, cm^{-1}): 2145 (w, $\nu_{C\equiv N}$), 2046 (w, $\nu_{C\equiv N}$), 1628 (vs, $\nu_{C=O}$), 1593 (vs), 1515 (m), 1473 (s), 1423 (m), 1356 (vs), 1138 (m), 847 (m), 761 (m), 730 (m), 691 (m), 510 (m).

$[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][M(bpb)(CN)_2]_2\cdot H_2O$ [M = Fe (3); Cr (4); Co (5)]. Dark brown block crystals of **3** and reddish brown block crystals of **4** and **5** were grown by the slow evaporation of a mixture prepared by carefully mixing a $CH_3CN-CH_3OH-H_2O$ solution (5 mL) of $Mn(phen)_2Cl_2$ (0.1 mmol), a CH_3OH solution (5 mL) of $K[M(bpb)(CN)_2]$ (0.1 mmol), and an aqueous solution

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Table 1. Crystallographic Data for Complexes **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
chemical formula	$FeMnC_{45}H_{34}N_{10}O_4Cl$	$CrMnC_{44}H_{32}N_{10}O_4Cl$	$Fe_2Mn_2C_{88}H_{58}N_{26}O_5$	$Cr_2Mn_2C_{88}H_5N_{26}O_5$	$Co_2Mn_2C_{88}H_{58}N_{26}O_5$	$Mn_2BC_{72}H_{53}N_{17}O_{0.5}$
fw	925.06	907.19	1781.18	1773.48	1787.34	1285.00
T/K	293	173	293	296	173	293
crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2/n$	$P2/n$	$P2/n$	$P\bar{1}$
a/Å	11.854(2)	11.822(2)	14.605(3)	14.2046(14)	14.1837(19)	13.378(3)
b/Å	14.723(3)	13.544(3)	10.919(2)	10.6938(10)	10.5486(14)	13.406(3)
c/Å	15.382(3)	15.676(3)	26.367(5)	26.233(2)	26.020(3)	18.851(4)
α/deg	114.33(3)	114.15(3)	90	90	90	88.99(3)
β/deg	101.89(3)	93.89(3)	94.89(3)	95.909(2)	95.632(5)	72.64(3)
γ/deg	100.11(3)	102.83(3)	90	90	90	81.04(3)
V/Å^3	2289.2(8)	2197.3(8)	4189.5(15)	3963.7(6)	3874.3(8)	3185.9(11)
Z	2	2	2	2	2	2
ρ_{calcd}/g cm^{-3}	1.342	1.371	1.412	1.486	1.532	1.340
F(000)	948	928	1820	1812	1824	1326
data/restraints/params	7934/2/577	7612/0/629	7331/0/562	14457/0/562	8405/0/558	10916/0/838
R1 [$I > 2\sigma(I)$]	0.0436	0.1226	0.0813	0.0620	0.0840	0.0940
wR2 (all data)	0.0988	0.2386	0.1956	0.1318	0.1850	0.1688

(2 mL) of NaN_3 (0.4 mmol) at room temperature. Yield: 35.2 mg (39.6%) for **3**, 32.5 mg (36.7%) for **4**, and 31.0 mg (35%) for **5**. Anal. Calcd for $C_{88}H_{58}N_{26}O_5Fe_2Mn_2$ (**3**): C, 59.34; H, 3.28; N, 20.45. Found: C, 59.29; H, 3.37; N, 20.28. Selected IR frequencies (KBr disk, cm^{-1}): 2121 (w, $\nu_{C\equiv N}$), 2109 (w, $\nu_{C\equiv N}$), 2051 (vs, $\nu_{N=N=N}$) 1627 (vs, $\nu_{C=O}$), 1582 (vs), 1516 (vs), 1468 (vs), 1422 (vs), 1356 (vs), 1142 (s), 958 (s), 855 (vs), 758 (s), 729 (s), 689 (m), 506 (m). Anal. Calcd for $C_{88}H_{58}N_{26}O_5Cr_2Mn_2$ (**4**): C, 59.60; H, 3.30; N, 20.53. Found: C, 59.52; H, 3.39; N, 20.29. Selected IR frequencies (KBr disk, cm^{-1}): 2173 (w, $\nu_{C\equiv N}$), 2117 (w, $\nu_{C\equiv N}$), 2051 (vs, $\nu_{N=N=N}$), 1632 (vs, $\nu_{C=O}$), 1588 (vs), 1517 (vs), 1471 (vs), 1422 (vs), 1358 (vs), 1147 (s), 961 (s), 855 (vs), 761 (s), 729 (s), 690 (m), 509 (m). Anal. Calcd for $C_{88}H_{58}N_{26}O_5Co_2Mn_2$ (**5**): C, 59.14; H, 3.27; N, 20.38. Found: C, 59.16; H, 3.34; N, 19.88. Selected IR frequencies (KBr disk, cm^{-1}): 2143 (vw, $\nu_{C\equiv N}$), 2119 (w, $\nu_{C\equiv N}$), 2050 (vs, $\nu_{N=N=N}$), 1631 (vs, $\nu_{C=O}$), 1593 (vs), 1517 (s), 1473 (s), 1422 (s), 1358 (vs), 1147 (m), 961 (w), 856 (s), 757 (s), 729 (s).

[Mn$_2$(phen)$_4$($\mu_{1,3}$-N$_3$)(N$_3$)$_2$]BPh$_4$·0.5H$_2$O (6). We obtained thin yellow single crystals of **6** in a sealed beaker at room temperature after ∼1 day by carefully mixing $Mn(phen)_2Cl_2$ (0.1 mmol) in CH_3CN-H_2O (8 mL, 7:1), NaN_3 (0.4 mmol) in H_2O (2 mL), and $NaBPh_4$ (0.1 mmol) in CH_3OH (2 mL). Yield: 12.0 mg (18.7%). Anal. Calcd for $C_{72}H_{53}N_{17}O_{0.5}Mn_2B$: C, 67.30; H, 4.16; N, 18.53. Found: C, 66.85; H, 4.20; N, 18.60. Selected IR frequencies (KBr disk, cm^{-1}): 2087 (vs, $\nu_{N=N=N}$), 2056 (vs, $\nu_{N=N=N}$), 1515 (s), 1423 (s), 846 (s), 729 (s), 638 (m), 612 (m).

X-ray Structure Determination. The crystal data are summarized in Table 1. The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms, and isotropic parameters were used for the hydrogen atoms. We added hydrogen atoms geometrically and refined them using a riding model.

Results and Discussion

Synthesis and General Characterization. All compounds reported herein are crystalline and reproducible. The dimeric complexes **1** and **2** were obtained by the reaction of equivalent molar $Mn(phen)_2Cl_2$ with K[M(bpb)(CN)$_2$] [M = Fe (**1**) and Cr (**2**)]. The formation of a dimeric structure is understandable when one considers that the presence of the bulky ligands phen and bpb^{2-} hinders the formation of trimeric or 1D chainlike complexes.[50] Therefore, we expected to replace the coordinating Cl$^-$ anion in **1** and **2** with the bridging anion N$_3^-$ with the hope of obtaining CN$^-$- and N$_3^-$-bridged complexes. Unexpectedly, the three EO azido-bridged binuclear Mn(II) complexes of **3**−**5** were formed, in which [M(bpb)(CN)$_2$]$^-$ only serves as a charge-balancing anion. In this context, we further tried other bulky anions, BPh$_4^-$, BF$_4^-$, and PF$_6^-$, instead of [M(bpb)(CN)$_2$]$^-$. A single EE azido-bridged binuclear Mn(II) complex (**6**) formed in the presence of BPh$_4^-$. However, only mononuclear Mn(phen)$_2$(N$_3$)$_2$ or [Mn(phen)$_2$(N$_3$)(H$_2$O)]ClO$_4$[45] was obtained when employing relatively smaller anions such as BF$_4^-$, ClO$_4^-$, and PF$_6^-$. Very recently, an oxalate-bridged binuclear Cr(III)−Mn(II) complex was synthesized by the reaction of [Cr(phen)(C$_2$O$_4$)$_2$]$^-$, $Mn(phen)_2Cl_2$, and NaN_3, in which the azide anion acts as a terminal ligand.[46] Therefore, it is intriguing to note that the formation of azido-bridged dimeric complexes and the bridging style of the azido group in these complexes are very subtle and are strongly dependent on the anions used.

The IR spectra of **1** and **2** in the range of 2040−2150 cm^{-1} exhibit two sharp peaks assigned to cyano stretching absorptions, which indicate the presence of bridging and nonbridging cyano ligands in [M(bpb)(CN)$_2$]$^-$. Moreover, the bridging cyano groups usually absorb at a higher frequency than do the terminal groups. For complexes **3**−**5**, the strong broad peaks centered at ∼2051 cm^{-1} that are assigned to the bridging azido stretching absorptions and the weak peaks at 2100−2200 cm^{-1} suggest the presence of CN$^-$ in these complexes. For complex **6**, a very strong splitting band at 2056 and 2087 cm^{-1} is consistent with a structure containing both EE bridging and terminal azido ligands.

Crystal Structures of Complexes 1 and 2. The labeling scheme for the crystal structures of complexes **1** and **2** are depicted in Figure 1, and some selected bond lengths and angles are presented in Table 2. The dimeric structures of **1**

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1** and **2**

	1	**2**		**1**	**2**
Mn−N(1)	2.202(2)	2.211(8)	M−C(1)	1.968(3)	2.116(9)
Mn−N(7)	2.249(3)	2.300(8)	M−C(2)	1.959(3)	2.105(9)
Mn−N(8)	2.303(2)	2.243(7)	M−N(3)	2.004(2)	2.080(8)
Mn−N(9)	2.322(3)	2.306(8)	M−N(4)	2.000(3)	2.086(7)
Mn−N(10)	2.258(2)	2.293(8)	M−N(5)	1.898(2)	1.969(7)
Mn−Cl	2.440(1)	2.434(3)	M−N(6)	1.879(3)	1.975(7)
C(1)−N(1)	1.145(3)	1.137(10)	C(2)−N(2)	1.137(4)	1.151(11)
Mn···M	5.304	5.404			
C(1)−N(1)−Mn	171.9(2)	166.4(7)	N(1)−C(1)−M	178.4(2)	175.2(7)
N(1)−Mn−Cl	93.57(7)	92.9(2)	N(2)−C(2)−M	179.4(3)	174.0(9)
C(2)−M−C(1)	169.82(12)	170.3(4)			

and **2** consist of $[Mn(phen)_2Cl]^+$ and $[M(bpb)(CN)_2]^-$ units (M = Fe or Cr) connected by one of the two cyano groups in the $[M(bpb)(CN)_2]^-$ building blocks.

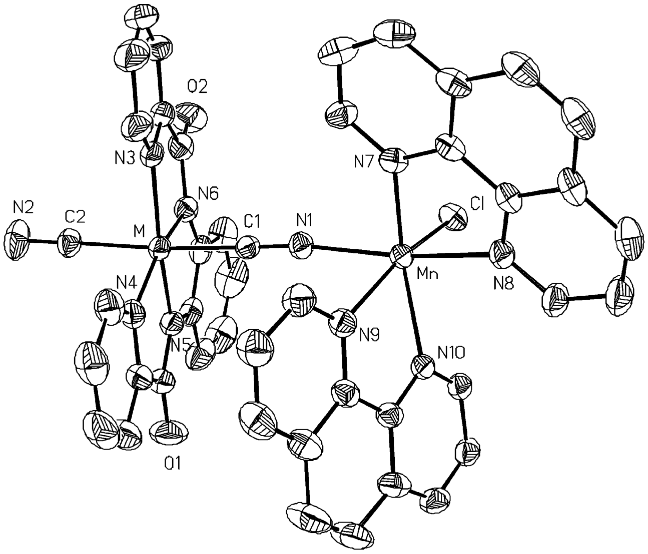

Figure 1. Crystal structure of dimeric $[Mn(phen)_2Cl][M(bpb)(CN)_2]$ complex **1** (M = Fe) or **2** (M = Cr). Hydrogen atoms and solvent molecules have been omitted for clarity.

The iron(III) and chromium(III) ions in complexes **1** and **2** are coordinated by four nitrogen atoms of bpb^{2-} and two cyano carbon atoms in a slightly distorted octahedral geometry. The Fe−C(1) (bridging cyano) and Fe−C(2) (unbridging cyano) bond distances in complex **1** are 1.965(2) and 1.955(2) Å, respectively, which are shorter than those in complex **2** [2.116(9) and 2.105(9) Å, respectively]. This is not unusual because the Cr(III) ion has larger ionic radii. The M−C≡N angles for both bridging and terminal cyano linkages in complex **1** are almost linear [178.4(2) and 179.4(3)°, respectively]. However, the M−C≡N angles in complex **2** are somewhat bent with 175.2(7) and 174.0(9)° for bridging M−C≡N and nonbridging M−C≡N linkages, respectively. The C(1)−M−C(2) bond angles in the two complexes are similar [169.82(12) and 170.3(4)° for **1** and **2**, respectively]. These data are consistent with those found in $[M(bpb)(CN)_2]^-$-containing complexes.[48,50]

The Mn(II) ions in the two complexes are also hexacoordinated with one chloride anion and one cyano nitrogen atom from $[M(bpb)(CN)_2]^-$ at cis positions and four nitrogen atoms from two cis-phen ligands yielding a MnN_5Cl octahedral surrounding. The $Mn-N_{cyano}$ bond distances are 2.202(2) Å for **1** and 2.211(8) Å for **2**, which are comparable to the average $Mn-N_{phen}$ bond distances of 2.284 Å for **1** and 2.285 Å for **2**. The Mn−Cl bond distances are a little longer, 2.4396(12) and 2.434(3) Å for **1** and **2**, respectively, which is similar to those found in $Mn(phen)_2Cl_2$.[47] The Mn−N≡C bond angles are in a bent fashion with 171.9(2)° for **1** and 166.4(7)° for **2**. The intramolecular Mn···Fe/Cr separations through the cyano bridges are 5.304 (**1**) and 5.407 Å (**2**), and the shortest intermolecular metal−metal distances are 6.618 and 6.865 Å for Fe···Fe and Cr···Mn, respectively.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **3**, **4**, and **5**

	3 (M = Fe)	**4** (M = Cr)	**5** (M = Co)
Mn(1)−N(11)	2.285(5)	2.2278(19)	2.228(6)
Mn(1)−N(14)	2.291(5)	2.2245(19)	2.230(6)
Mn(1)−N(7)	2.319(4)	2.256(2)	2.274(5)
Mn(1)−N(8)	2.307(4)	2.2531(18)	2.233(5)
Mn(1)−N(9)	2.286(4)	2.2518(19)	2.247(5)
Mn(1)−N(10)	2.298(4)	2.256(2)	2.257(5)
M(1)−C(1)	2.011(5)	2.098(2)	1.927(6)
M(1)−C(2)	2.005(6)	2.075(3)	1.907(6)
M(1)−N(3)	2.071(4)	2.0869(19)	1.981(5)
M(1)−N(4)	1.925(4)	1.9712(17)	1.886(5)
M(1)−N(5)	1.946(4)	1.9661(18)	1.901(5)
M(1)−N(6)	2.044(4)	2.0823(18)	1.986(5)
Mn(1)···Mn(1A)[a]	3.541	3.473	3.480
Mn(1)−N(11)−Mn(1A)[a]	101.6(3)	102.44(12)	102.7(4)
Mn(1)−N(14)−Mn(1A)[a]	101.2(3)	102.65(12)	102.5(4)
N(14)−N(15)−N(16)	180.000(3)	180.000(2)	180.000(4)
N(11)−N(12)−N(13)	180.000(6)	180.000(2)	180.000(6)
M(1)−C(1)−N(1)	179.4(5)	179.1(2)	178.1(6)
M(1)−C(2)−N(2)	179.1(6)	177.9(3)	176.8(6)
C(1)−M(1)−C(2)	169.0(2)	170.73(9)	175.9(3)

[a] A: $-x + 1/2, y, -z + 1/2$.

Crystal Structures of Complexes 3−5. Selected bond lengths and angles for the three isostructural complexes are presented in Table 3, and the structural drawing of $[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][M(bpb)(CN)_2]_2\cdot H_2O$ [M = Fe (**3**), Cr (**4**), Co (**5**)] is shown in Figure 2. The complexes feature a doubly EO azido-bridged Mn(II) dimer with two free $[M(bpb)(CN)_2]^-$ units as charge-balancing anions.

Each Mn(II) ion in the two dimers exhibits a distorted-octahedral coordination sphere with four nitrogen atoms from two phen ligands and the other two cis- nitrogen atoms from two EO azido bridges. The four atoms involved in bridging, Mn(1), N(11), Mn(1A), and N(14), form a perfect plane. The

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(50) Ni, Z.-H.; Kou, H.-Z.; Zhao, Y.-H.; Zheng, L.; Wang, R.-J.; Cui, A.-L.; Sato, O. *Inorg. Chem.* **2005**, *44*, 2050.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **6**

Mn(1)−N(1)	2.270(5)	Mn(2)−N(5)	2.258(5)	N(9)−N(10)	1.184(8)
Mn(1)−N(2)	2.245(5)	Mn(2)−N(6)	2.285(6)	N(10)−N(11)	1.159(8)
Mn(1)−N(3)	2.292(5)	Mn(2)−N(7)	2.257(5)	N(12)−N(13)	1.153(8)
Mn(1)−N(4)	2.234(6)	Mn(2)−N(8)	2.269(5)	N(13)−N(14)	1.139(8)
Mn(1)−N(11)	2.158(6)	Mn(2)−N(9)	2.183(6)	N(15)−N(16)	1.083(8)
Mn(1)−N(15)	2.137(7)	Mn(2)−N(12)	2.111(6)	N(16)−N(17)	1.182(9)
Mn(1)···Mn(2)	5.895				
N(15)−Mn(1)−N(11)	96.2(3)	N(16)−N(15)−Mn(1)	126.2(7)	N(10)−N(11)−Mn(1)	133.9(6)
N(12)−Mn(2)−N(9)	93.3(3)	N(13)−N(12)−Mn(2)	128.3(5)	N(10)−N(9)−Mn(2)	124.0(5)
N(11)−N(10)−N(9)	177.2(7)	N(14)−N(13)−N(12)	175.9(9)	N(15)−N(16)−N(17)	176.8(10)
N(11)−Mn(1)−N(1)	87.6(2)	N(11)−Mn(1)−N(2)	94.8(2)	N(11)−Mn(1)−N(3)	165.8(3)
N(11)−Mn(1)−N(4)	93.5(3)	N(9)−Mn(2)−N(5)	92.0(2)	N(9)−Mn(2)−N(6)	164.7(2)
N(9)−Mn(2)−N(7)	99.7(2)	N(9)−Mn(2)−N(8)	87.6(2)		

Mn(1)−N(11)−Mn(1A) and Mn(1)−N(14)−Mn(1A) bond angles in the EO mode are in the range of 101.2(3)−102.65(12)°, which is comparable to the previously published results (99.91−106.5°) for this kind of bridging mode.[42−44] Significantly, the Mn(1)−N(11) and Mn(1)−N(14) bond distances for complex **3** of 2.285(5) and 2.291(5) Å, respectively are somewhat larger than those of complexes **4** [2.2278(19) and 2.2245(19) Å] and **5** [2.228(6) and 2.230(6) Å]. The bridging azido ligands are strictly linear with N(11)−N(12)−N(13) and N(14)−N(15)−N(16) equal to 180°. The intradimer Mn(1)···Mn(1A) distances are 3.541(2) Å for **3**, 3.473(1) Å for **4**, and 3.480(2) Å for **5**. Overall, the structural data of the Mn(II) coordination environments for complexes **4** and **5** are very similar but are slightly different from those for complex **3**.

Crystal Structures of Complex 6. A unique feature of the structure for complex **6** is the single EE azido bridge between the two Mn(II) ions (Figure 3). Some selected bond lengths and angles for the two complexes are presented in Table 4. To our knowledge, this complex is the first binuclear Mn(II) complex with a single azido bridging group in a μ-1,3 or EE fashion. The other two azido ligands are terminal. This kind of bridging mode is reminiscent of the first singly EE azido-bridged dimeric 4*f* complex $Gd_2(phen)_4(\mu_{1,3}\text{-}N_3)(N_3)_5(H_2O)$.[51] The Mn−N−N bond angles are 133.9(6) and 124.0(5)° for Mn(1)−N(11)−N(10) and Mn(2)−N(9)−N(10), respectively. The $Mn-N_{bridging}$ bond distances are 2.158(6) Å for Mn(1)−N(11) and 2.183(6) Å for Mn(2)−N(9) and are somewhat larger than those of the $Mn-N_{nonbridging}$ bond distances [2.137(7) Å for Mn(1)−N(15) and 2.111(6) Å for Mn(2)−N(12)]. The noncentrosymmetric nature of the cation gives rise to the Mn(1)−N(11)−N(10)−N(9)−Mn(2) torsion angle of 127.2°. The Mn···Mn intradimer distance is 5.895 Å, and the shortest intermolecular distance is 8.940 Å.

Magnetic Properties of Complexes 1 and 2. The magnetic properties of the two cyano-bridged complexes have been investigated because binuclear complexes are the best candidates for accurately evaluating the magnetic coupling strength and furthering the magneto-structural correlations. However, the examples of cyano-bridged dimeric complexes, especially the cyano-bridged Mn(II)−Fe(III) and Mn(II)−Cr(III) binuclear complexes, are rather scarce although there are some tri-, penta- and heptanuclear species reported.[52−55]

The temperature dependences of the magnetic susceptibilities for **1** and **2** measured in the temperature range of 5−300 K are illustrated in Figure 4. The room-temperature $\chi_m T$ values of 4.79 emu K mol^{-1} for **1** and 6.325 emu K mol^{-1} for **2** are close to the spin-only values of 4.75 and 6.25 emu K mol^{-1} expected for the uncoupled spin systems S_{Fe}, S_{Mn} = $^1/_2$, $^5/_2$ and S_{Cr}, S_{Mn} = $^3/_2$, $^5/_2$, respectively, assuming g = 2.00. When the temperature is lowered, $\chi_m T$ decreases gradually until ~50 K for **1** and 75 K for **2** and then sharply decreases to 3.46 and 1.34 emu K mol^{-1} at 5 K for **1** and **2**, respectively. This is characteristic of antiferromagntic cou-

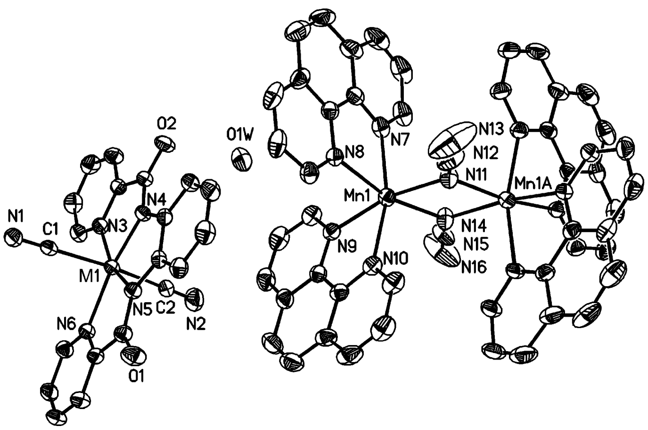

Figure 2. Crystal structure of $[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][M(bpb)(CN)_2]_2\cdot H_2O$ [M1 = Fe1 (**3**); M1 = Cr1 (**4**); M1 = Co1 (**5**)]. Hydrogen atoms have been omitted for clarity.

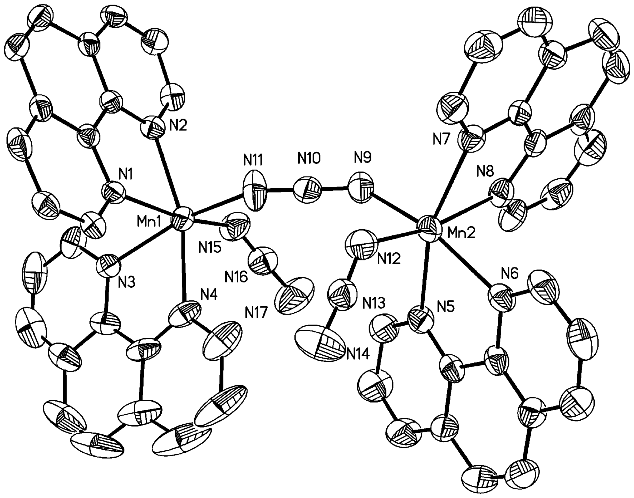

Figure 3. Structure of the dimeric $[Mn_2(phen)_4(N_3)_2(\mu_{1,3}\text{-}N_3)]^+$ cation in complex **6**. Hydrogen atoms and the BPh_4^- anion have been omitted for clarity.

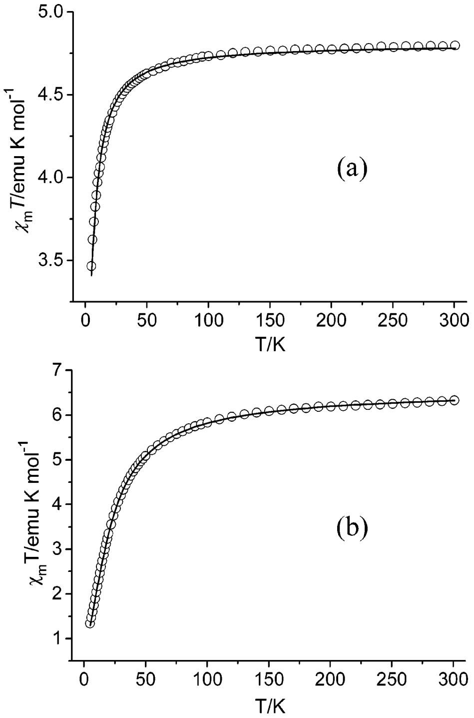

Figure 4. Temperature dependencies of $\chi_m T$ for **1** (a) and **2** (b). The solid lines represent the best fit based on the parameters discussed in the text.

pling in the two cyano-bridged dimeric complexes. The magnetic susceptibilities obey the Curie−Weiss law with a negative Weiss constant $\theta = -2.16$ K and Curie constant $C = 4.83$ emu K mol^{-1} for **1**, and $\theta = -15.7$ K and $C = 6.66$ emu K mol^{-1} for **2**, which also confirms the presence of overall antiferromagnetic interactions in the two complexes. On the basis of the dimeric model, the magnetic susceptibilities of complexes **1** and **2** can be fitted accordingly by the following expressions derived from the isotropic exchange spin Hamiltonian $\hat{H} = -J\hat{S}_{Mn}\hat{S}_{Fe}$ for **1** (eq 1) and $\hat{H} = -J\hat{S}_{Mn}\hat{S}_{Cr}$ **2** (eq 2):

$$\chi_m = \frac{Ng^2\beta^2}{kT}\cdot\frac{10\exp(-3J/kT) + 28}{5\exp(-3J/kT) + 7} \tag{1}$$

$$\chi_m = \frac{Ng^2\beta^2}{kT}\left[\frac{A}{B}\right] \tag{2}$$

in which $A = 2 + 10\exp(4J/kT) + 28\exp(10J/kT) + 60\exp(18J/kT)$, and $B = 3 + 5\exp(4J/kT) + 7\exp(10J/kT) + 9\exp(18J/kT)$.

The best-fit parameters obtained are $J = -2.68(3)$ cm^{-1}, $g = 2.01(1)$, and $R = \sum(\chi_{obsd}T - \chi_{cald}T)^2/\sum(\chi_{obsd}T)^2 = 7.3 \times 10^{-4}$ for complex **1** and $J = -4.55(1)$ cm^{-1}, $g = 2.05(1)$, and $R = 5.0 \times 10^{-5}$ for complex **2**.

In general, the magnetic coupling between high-spin Mn(II) and Cr(III) or low-spin Fe(III) through cyano bridging is antiferromagnetic,[21b,21d,52−54,56,57] resulting from a net overlap of the magnetic orbitals through the π t_{2g}-t_{2g} pathways [$t_{2g}{}^3e_g{}^2$ and $t_{2g}{}^3$ or $t_{2g}{}^5e_g{}^0$ configurations for Mn(II) and Cr(III) or Fe(III), respectively]. The J value ($-2.68(3)$ cm^{-1}) for **1** can be compared with those for the centrosymmetric trinuclear complexes [{Fe(bipy)(CN)$_4$}$_2$Mn(H$_2$O)$_4$]•4H$_2$O[52] ($J = -1.8$ cm^{-1}) and [{(Tp)Fe(CN)$_3$}$_2$Mn(CH$_3$OH)$_4$]•2CH$_3$OH[53] ($J = -15.2$[53b] or -4.38[53a] cm^{-1}), the tetranuclear [{(Tp)Fe(CN)$_3$}$_2$Mn$_2$(4,4′-bpy)$_2$](ClO$_4$)$_2$·4MeCN[53b] ($J = -4.58$ cm^{-1}), and the pentanuclear [{Mn$_3$(MAC)$_3$(H$_2$O)$_2$}{Fe(CN)$_6$}$_2$]•6H$_2$O•2CH$_3$OH[54] (MAC = /2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene) ($J \approx -2$ cm^{-1}). The relatively weaker antiferromagnetic coupling in complex **2** [$J = -4.55(1)$ cm^{-1}] compared with cyano-bridged heptanuclear CrMn$_6$ clusters {$J = -10.0$ cm^{-1} for [Cr{CN−Mn(dmptacn)}$_6$][Cr(CN)$_6$](ClO$_4$)$_6$•6H$_2$O (dmptacn = 1,4-bis(2-methylpyridyl)-1,4,7-triazacyclononane),[55a] $J = -12.4$ cm^{-1} for [{Cr(bipy)(CN)$_4$}$_2$Mn(H$_2$O)$_4$]•4H$_2$O,[55b] $J = -16.0$ for [{Mn(L)(NC)}$_6$Cr]$^{9+}$ (L = *N*,*N*,*N*′-[tris(2-pyridylmethyl)-*N*′-methylethane]1,2-diamine),[55c] $J = -18$ cm^{-1} for [Cr{CN−Mn(tetren)}$_6$][Mn(tetren)(H$_2$O)](ClO$_4$)$_{22}$},[55d] and a 1D chainlike complex, {Mn(N$_3$)(CH$_3$OH)[Cr(phen)(CN)$_4$]}•CH$_3$OH[30] ($J = -9.4$ cm^{-1}), can be ascribed to the Mn•••Cr separation through the bridging cyano in **2** being somewhat longer (5.404 Å) than those in the other complexes (5.318−5.368 Å). It should be noted that because of the employment of different Hamiltonian operators, the J values in the literature have been doubled for comparison.

Magnetic Behavior of Complexes 3−5. The $\chi_m T$ versus T plots (5−300 K) of **3**−**5** are shown in Figure 5. When cooled, $\chi_m T$ increases smoothly, reaching a maximum value of 15.24 emu K mol^{-1} at 5.9 K for **3** [expected maximum value is 15.75 emu K mol^{-1} for a ferromagnetic Mn$_2$ dimer with two isolated low-spin Fe(III) units], 18.16 emu K mol^{-1} at 5.5 K for **4** [expected maximum value is 18.75 emu K mol^{-1} for a ferromagnetic Mn$_2$ dimer with two isolated Cr(III) units], and 14.5 emu K mol^{-1} at 6 K for **5** [expected maximum value is 15.0 emu K mol^{-1} for a ferromagnetic Mn$_2$ dimer with two isolated diamagnetic Co(III) units] and then sharply decreases. The magnetic susceptibilities (20−300 K) of complexes **3**−**5** obey the Curie−Weiss law with

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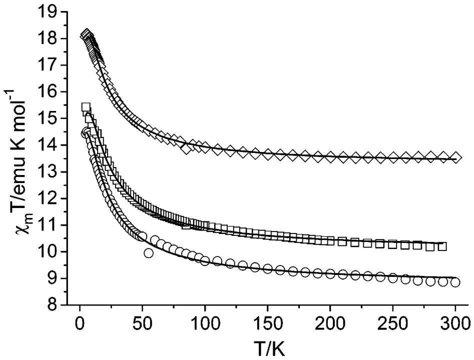

Figure 5. Temperature dependencies of $\chi_m T$ for **3** (□), **4** (◇) and **5** (○). The solid lines represent the best fit based on the parameters discussed in the text.

a positive Weiss constant $\theta = +8.36$ K and Curie constant $C = 9.47$ emu K mol^{-1} for **3**, $\theta = +2.90$ K and $C = 13.42$ emu K mol^{-1} for **4**, and $\theta = +8.72$ K and $C = 8.70$ emu K mol^{-1} for **5**. The positive Weiss constants and the shape of the $\chi_m T$ curves for the three complexes are typical of ferromagnetic coupling between the EO azido-bridged Mn(II)−Mn(II) ions. The abrupt decrease at low temperatures may be due to the operation of weak intermolecular antiferromagnetic interactions and/or zero-field-splitting effect.

The magnetic susceptibility data of **3**−**5** can be analyzed by using a Mn_2 dimer model together with the contribution from the isolated M(III) ions. The expression for the magnetic susceptibility (χ_d) of the Mn(II) dimer ($\hat{H} = -J\hat{S}_{Mn1}\hat{S}_{Mn2}$), derived from Van Vleck's equation, is written as

$$\chi_d = \frac{2Ng^2\beta^2}{kT}\left[\frac{A}{B}\right]$$

in which $A = 55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)$, and $B = 11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)$. And the final molar magnetic susceptibility (χ_m/Mn_2M_2) is in the form

$$\chi_m = \chi_d + 2 \times \frac{Ng^2\beta^2}{3kT} S_M(S_M + 1)$$

in which $S_{Co} = 0$ for complex **5**.

The least-squares fit of the experimental data in the whole temperature range to the above expression gives the following parameters: $J = 1.20(2)$ cm^{-1}, $g = 2.05(1)$, $zJ' = -0.015(1)$ cm^{-1}, and $R = 9.9 \times 10^{-5}$ for **3**; $J = 1.10(1)$ cm^{-1}, $g = 2.05(1)$, $zJ' = -0.012(1)$ cm^{-1}, and $R = 6.2 \times 10^{-5}$ for **4**; and $J = 1.27(2)$ cm^{-1}, $g = 2.00(1)$, $zJ' = -0.0043(9)$ cm^{-1}, and $R = 9.3 \times 10^{-4}$ for **5**.

The ferromagnetic interactions in the two doubly EO azido-bridged complexes can be better explained on the basis of the spin-polarization model[40] and a density functional theory calculation (DFT).[39] According to the spin-polarization model, the in-plane π_g-orbital (highest occupied molecular orbital) of N_3^- has a node on the central nitrogen atom, and the two electrons with the α and β spins are localized around the two terminal nitrogen atoms in this orbital. For azido in EO bridging mode, the electron on the bridging nitrogen atom (α spin) is partially delocalized in φ_A toward the two d_{xy} metal orbitals, and consequently the unpaired electrons occupying the d_{xy} orbitals are likely to have a β spin larger than $^1/_2$, which favors ferromagnetic interactions. The DFT calculation indicates that the delocalization of the unpaired electrons at $d_{x^2-y^2}$-type orbitals toward the donor atoms decreases in the order Cu > Ni > Mn, whereas the spin polarization increases in the same direction because of the increased number of unpaired electrons. As a result, Cu(II)−, Ni(II)−, and Mn(II)−azido systems manifest very different magneto-structural correlations. For Cu(II) dimers, theoretical calculation indicates that the ferromagnetic coupling decreases as the bridging angle (θ) increases from a maximum at approximately $\theta = 85°$, and the magnetic interaction is actually reversed to antiferromagnetic coupling when the Cu−N−Cu angle is larger than 104°. For Ni(II) dimeric complexes, the interaction is predicted to be ferromagnetic for the entire range of Ni−N−Ni (θ) angles: J increases with increasing θ until θ reaches ∼104°, and then J decreases with increasing θ. However, for the Mn(II) dimeric complex, the DFT calculation suggests a trend of magnetic interaction contrary to that of Cu(II) complexes, namely, the value of J increases with increasing θ in the global range, and a crossover from ferro- to antiferromagnetic interaction is predicted at $\theta \approx 98°$. The experimental results previously published strongly support the above prediction for Cu(II) and Ni(II) dimeric complexes. Very recently, the theoretical prediction for the Mn(II) system has been confirmed.[44b] The results in this work and the other five available magnetism examples further indicate that the ferromagnetic interaction increases with the increase of the Mn−N−Mn bond angles, as shown in Table 5. Figure 6 shows the J vs θ (the Mn−N−Mn bond angle) correlationship on the basis of the EO azido-bridged Mn(II) dimers listed in Table 5. The abnormity of **3** may be due to the effect of free low-spin iron(III) ions in the complex. Because of the orbital contribution to the magnetic susceptibility for Fe(III), the J value might be overrated during the fitting. The least-squares fit based on the data of the six compounds (except compound **3**) gives the correlation of $J = 0.614\theta - 61.9$ (cm^{-1}), in which θ is the Mn−N−Mn bond angle (°). This equation is similar to that reported in the literature of $J = 0.64\theta - 64.5$ (cm^{-1}),[58] which was derived on the basis of four data points.[44b]

Magnetic Properties of Complex 6. The magnetic susceptibilities of the complex have been measured in the temperature range 5−300 K as shown Figure 7. The $\chi_m T$ product at room temperature is 7.83 emu K mol^{-1}, which is lower than the spin-only value of 8.75 for the uncoupled Mn(II) dimeric system in which $g = 2.00$. A gradual decrease in $\chi_m T$ is observed as the temperature is decreased, and the $\chi_m T$ value reaches 0.62 emu K mol^{-1} at 5 K, indicating that there is a dominant intermetallic antiferromagnetic interaction in complex **6**. The magnetic susceptibilities obey the Curie−

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(58) The linear fit equation shown in Figure 7 of ref 44b is incorrect, and the equation given herein is consistent with the shape of the fitting line.

Table 5. Comparison of Mn(II) Dimers with Doubly EO Azido Bridging Groups[a]

compounds	$Mn-N_{azido}$ Å	Mn⋯Mn Å	Mn−N−Mn deg	J cm^{-1}	refs
$[Mn_2(terpy)_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2]\cdot 2H_2O$	2.182(3)	3.525	104.6(1)	2.43	43
$[Mn_2(L2)_2(\mu_{1,1}\text{-}N_3)_2](ClO_4)_2$	2.240(3)	3.537(1)	104.29(11)	2.04(3)	44b
$[Mn_2(L3)_2(\mu_{1,1}\text{-}N_3)_2](ClO_4)_2$	2.248(4)	3.534(1)	103.58(19)	1.75(2)	44b
$[Mn_2(2,2'\text{-}dpa)_2(N_3)_2(\mu_{1,1}\text{-}N_3)_2]$	2.237(2)	3.504	103.11(10)	1.12	44a
$[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][Co(bpb)(CN)_2]_2\cdot H_2O$	2.228(6)	3.480	102.6(4)	1.27	this work
$[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][Cr(bpb)(CN)_2]_2\cdot H_2O$	2.226(2)	3.473	102.55(12)	1.10	this work
$[Mn_2(L1)_2(\mu_{1,1}\text{-}N_3)_2](ClO_4)_2$	2.235(3)	3.493(1)	102.12(12)	0.77(1)	44b
$[Mn_2(phen)_4(\mu_{1,1}\text{-}N_3)_2][Fe(bpb)(CN)_2]_2\cdot H_2O$	2.288(5)	3.541	101.4(3)	1.20	this work

[a] The Mn−N bond distances, Mn⋯Mn separations, and Mn−N−Mn bond angles are average values.

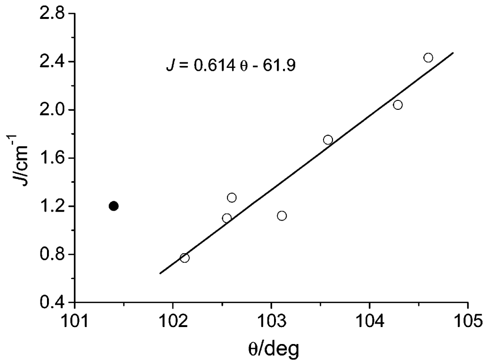

Figure 6. Plot of J vs Mn−N−Mn bond angle (θ) for EO azido-bridged dimeric Mn(II) compounds. The straight line represents the best fit based on the equation shown in the plot [the data (●) for complex **3** are excluded from the fit].

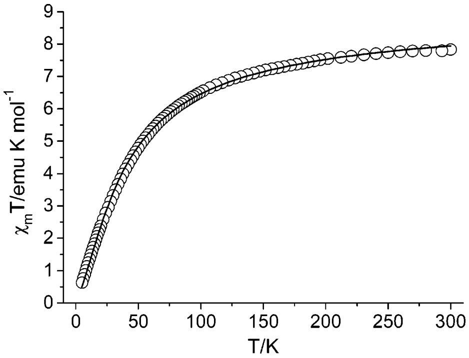

Figure 7. Temperature dependencies of $\chi_m T$ for **6**. The solid line represents the best fit based on the parameters discussed in the text.

Weiss law with a negative Weiss constant $\theta = -39.1$ K and Curie constant $C = 8.96$ emu K mol^{-1}, which also confirms the presence of dominant antiferromagnetic interactions in the complex. Using the magnetic expression for the Mn(II) dimer ($\hat{H} = -J\hat{S}_{Mn1}\hat{S}_{Mn2}$), we obtained the following best-fit parameters: $J = -2.29(4)$ cm^{-1}, $g = 1.99(1)$, $zJ' = -0.70(7)$ cm^{-1}, and $R = 1.1 \times 10^{-4}$.

Similar to most of the single EE azido-bridged Ni(II) and Cu(II) dimeric complexes,[26,41a] the Mn(II) binuclear complex in this work shows intradimer antiferromagntic interaction, consistent with that of the EE azido-bridged Mn(II) polymers.[25b,e,f] According to the spin-polarization model,[40] when N_3^- bridges in an EE mode, the α electron is partially delocalized in φ_A toward a d_{xy} metal orbital, and the β electron is symmetrically delocalized toward another d_{xy} metal orbital. As a result, the unpaired electrons occupying the magnetic orbitals are likely to have a β spin larger than $^1/_2$ around the former metal center and an α spin larger than $^1/_2$ around the latter metal center, facilitating the antiferromagnetic coupling. On the basis of this theory and the magnetic properties of some EE azido-bridged Mn(II) polymers, it has been proven that the EE azido bridge always transmits antiferromagnetic coupling and that the magnitude of the magnetic coupling is related to the dihedral angle, τ, which is defined by the angle between two Mn−N−N−N planes (also the Mn−N−N−N−Mn torsion angle). The larger the τ value is, the weaker the magnetic exchange coupling is. The absolute J value for complex **6** is small and comparable to that of the EE azido-bridged polymeric complexes.[22c,25b,59] Because of the shortage of examples with single EE azido bridges, the magneto-structural correlation cannot be done at this stage.

Conclusions

In this work, we have successfully prepared the first single EE azido-bridged Mn(II) dimeric complex and three novel doubly EO azido-bridged Mn(II) binuclear complexes, as well as two new cyano-bridged Mn(II)−Fe(III) and Mn(II)−Cr(III) dimeric complexes using $[Mn(phen)_2]^{2+}$ and $[M(bpb)(CN)_2]^-$ building blocks. From a preparation standpoint, it is important to reemphasize that the employment of the bulky $[Cr(phen)(C_2O_4)_2]^-$ anion yields the oxalate-bridged $[(phen)(C_2O_4)Cr(\mu\text{-}C_2O_4)Mn(phen)_2(N_3)]\cdot H_2O$ binuclear complex,[46] whereas the $[M(bpb)(CN)_2]^-$ anions can induce the formation of doubly EO azido-bridged Mn(II) dimers. In addition, the use of the bulky BPh_4^- anion gives a binuclear Mn(II) complex bridged by a single EE azido group, whereas BF_4^-, ClO_4^-, and PF_6^- only produce mononuclear $Mn(phen)_2(N_3)_2$ or $[Mn(phen)_2(N_3)(H_2O)]ClO_4$. This research suggests that new azido-bridged dimeric complexes might be synthesized via the careful selection of counteranions. Therefore, further work should be done to clarify the subtle reaction mechanism of azido-bridged Mn(II) complexes and to elucidate magneto-structural correlations.

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Supporting Information Available: An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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